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(71) Applicant: Hitachi, Ltd.
Chiyoda-ku, Tokyo 101-8010 (JP)

(72) Inventors:
- Kitsunai, Hiroyuki
Niihari-gun, Ibaraki 315-0055 (JP)
- Tsumaki, Nobuo
Ushiku-shi, Ibaraki 300-1236 (JP)
- Kakuta, Shigeru
Yokohama-shi, Kanagawa 244-0817 (JP)
- Nojiri, Kazuo
Higashimurayama-shi, Tokyo 189-0012 (JP)
- Takahashi, Kazue
Kudamatsu-shi, Yamaguchi 744-0006 (JP)

(74) Representative: Paget, Hugh Charles Edward et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

# (54) Plasma treatment method and manufacturing method of semiconductor device

(57) The dry cleaning method is capable of removing deposition films left adhered to the inner walls of semiconductor manufacturing apparatus i.e. removing dust production sources. To this end, the dry cleaning process includes a step of removing either ion sputtered matter or products of the internal member materials of the apparatus or chemical compounds of such apparatus internal member materials and of an etching gas, in addition to a step of removing etching reaction products. It thus becomes possible to eliminate dust generation due to peeling off of deposition films with an increase in number of wafers being processed, which in turn increases the manufacturing yield and working efficiency of the manufacturing apparatus.

EP 0 871 211 A2

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## Description

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates a method for dry-cleaning the interior of semiconductor manufacturing apparatus for use in performing microfabrication or film formation on substrates during the manufacturing processes of semiconductor devices. In addition, the invention also relates to a method for manufacturing semiconductor devices by use of semiconductor manufacturing apparatus with its inside cleaned.

#### 2. Description of the Prior Art

In manufacturing processes of semiconductor devices, attachment or adhesion of dusts (contaminants) to substrates under manufacture raises pattern defects of target devices, which in turn reduces the production yield during manufacturing processes.

In currently available manufacturing processes some processes are becoming more important, including dry etching technology using plasma, chemical vapor deposition (CVD) and the like. More specifically, the processes are to perform microfabrication such as film formation, etching and the like by utilizing plasma reaction of various kinds of gases as introduced into the apparatus. During execution of these processes, deposition films tend to be left adhered also to the inner walls of manufacturing apparatus used, other than a target substrate being subjected to such microfabrication. One example is that in the dry etching, certain deposition films can be adhered to the inner walls of the apparatus due to decomposition or combination of etching gases within a plasma and also due to generation of secondary etching products during etching. As wafers to be processed increase in number causing the film thickness to increase accordingly, such deposition films badly behave to partly peel off therefrom and then act as dusts or contaminants which raise the cause of pattern defects of devices manufactured. Accordingly, it should be required that such adhesion deposits be removed away periodically.

Conventionally, one typical approach to removal of such adhesion deposits is the so-called wet cleaning technology-i.e. wiping out them by using catalytic substance such as alcohol or pure water or the like while letting the apparatus be exposed to the atmosphere. Another prior known approach is a dry cleaning scheme using a combination of chlorine-based gas and fluorine-based gas as disclosed, for example, in Published Unexamined Japanese Patent Application (PUJPA) No. 3-62520. A further prior art approach is a dry cleaning technique using a plasma of a mixture of oxygen gas and chlorine gas as disclosed for example in PUJPA No. 7-508313.

Unfortunately, the prior art approaches are encountered with serious problems which follow.

First, with regard to the wet cleaning approach, it has been required that the apparatus be disassembled every time it is exposed to the atmosphere at constant time intervals; in addition thereto, the vacuum evacuation procedure is required after completion of every wet cleaning process. Obviously, this would result in operation termination of the apparatus for an increased time duration every time the cleaning treatment is done, which in turn leads to a noticeable decrease in working efficiency of the apparatus while reducing the throughput thereof.

Second, regarding the approach disclosed in PUJPA No. 3-62520, the material to be etched is an alloy containing therein Al and W, and therefore the technique disclosed therein is featured in that the cleaning steps for a plurality of etching objects are combined together in order to remove away Al's etching products as well as W's etching products. The third prior art approach employing the dry cleaning technique as taught by PUJPA No. 7-508313 is featured by removing what is called the reaction products as originated from chemical reaction between the to-be-etched material and an etching gas used or between a photoresist (carbon) employed as a mask layer material for etching and the etching gas or still alternatively due to polymeric bodies of the etching gas.

These prior art approaches are completely silent about cleaning of either ion sputtered matter or "residue" of the materials of internal members of the apparatus or chemical compounds of the apparatus internal member materials and an etching gas used, although these prior art documents involve teachings as to how to clean up certain products resulting from chemical reaction between the etching gas and those materials left on wafer substrates, such as to-be-etched materials, mask materials and the like.

In the etching apparatus a plasma created by the etching gas attempts to etch the substrate surface to be etched and simultaneously sputter the apparatus internal member materials also, which might result in attachment and adhesion of certain materials onto the inner walls of the apparatus, which materials may include in addition to etching reaction products either ion-sputtered matter of such apparatus internal member materials or chemical compounds of the apparatus internal member materials and of the etching gas employed.

In other words, the prior art dry cleaning methodology is faced with a serious problem left unsolved: it is not possible to fully remove away the ion sputtered matter or products of the apparatus internal member materials or the chemical compounds of such apparatus materials and etching gas, which results in generation of contaminants due to lamination of resultant non-removed materials left on the inner walls of the apparatus.

## SUMMARY OF THE INVENTION

It is therefore an object of the present invention to avoid the problems associated with the prior art, and also to provide a dry cleaning method capable of effectively removing away any deposition films left adhered to the inner walls of manufacturing apparatus, more specifically, capable of successfully removing any possible dust production sources.

The invention provides a specific dry etching process which includes the steps of removing etching reaction products, and removing either ion sputtered constituents of those materials of the internal structure members of manufacturing apparatus or chemical compounds of such apparatus materials and an etching gas used.

The invention also provides a dry cleaning process which makes use of a chosen gas that contains therein a material having its interatomic bonding energy with respect to elements constituting a gas for use during an etching and a cleaning step, which energy is greater in value than the atomic bonding energy between elements constituting a material to be etched and elements constituting a gas or gases used during the etching and cleaning processes.

The invention further consists in employing for the dry cleaning process a specific kind of gas which contains therein a material that has its interatomic bonding energy with respect to elements constituting gases for use in the etching and cleaning steps, which energy is greater in value than the interatomic bonding energy between elements constituting the apparatus internal member materials and those elements constituting gases used in the etching and cleaning processes.

These and other features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing semiconductor manufacturing apparatus incorporating the principles of the present invention.

Fig. 2A and 2B are diagrams illustrating, in cross-section, two major steps in the manufacture of a semiconductor wafer in accordance with a first embodiment of the invention.

Fig. 3A and 3B are diagrams depicting in cross-section two major steps in the manufacture of a semiconductor wafer in accordance with a second embodiment of the invention.

Fig. 4A and 4B are diagrams showing in cross-section two major steps in the manufacture of a semiconductor wafer in accordance with a third embodiment of the invention.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Some preferred embodiments of the dry cleaning methodology of the present invention will be explained in detail with reference to the accompanying drawings.

Fig. 1 illustrates a configuration of microwave etching apparatus adapted for use in performing the dry cleaning method in accordance with the present invention. In this drawing, reference numeral 1 designates a silicon wafer (substrate) to be subjected to microfabrication; numerals 3 and 4 denote a quartz bell jar and a main chamber for establishment of the vacuum environment required. 10 indicates an exhaust port for vacuum evacuation whereas 15 denotes a gas introduction section for introduction of a gas or gases used in etching or dry cleaning. 9 is a substrate stage for rigid support of a wafer under manufacture; 8 is a clamper for clamping the wafer. This clamper may typically be made of ceramics including, but not limited to, alumina ceramics. Electrostatic suction force may be used to rigidly support the wafer on the substrate stage 9. 7 designates an Earth plate; 11 denotes a high-frequency power supply for application of a radiofrequency (RF) bias voltage between the Earth plate 7 and wafer stage 9.

The microwave etching apparatus shown herein is first subject to introduction of a chosen gas for use in generating a plasma after completion of high vacuum evacuation. Then, microwaves 14 are excited by a magnetron (not shown) and are then introduced via the waveguide 5 into the quartz bell jar 3 (processing room) causing a gas in the processing room to transform into a plasma by electronic cyclotron resonance (ECR) with a magnetic field as created by the solenoid 6 disposed around the processing room, which plasma is used to effectuate an intended etching treatment. The RF bias voltage is applied by the high-frequency power supply 11 between the Earth plate 7 and wafer stage 9 for the purpose of performing an anisotropic etching by attraction of ions thereto.

At this time certain reaction products formed as secondary products of the etching process can be attached and stacked onto the constituent components of the processing room, such as the quartz bell jar 3, main chamber 4, exit 15 of the gas introduction section, clamper 8 and others, which would result in formation of more than one deposition film 13. As wafers under processing increase in number letting such deposition film 13 likewise increase in thickness, this film behaves to peel off from the inner walls then badly behaving as dusts or contaminants which can cause pattern defects of resultant devices manufactured.

Suppose for example that a silicon oxide film ($SiO_2$) 17 for use as a dielectric film shown in Fig. 2 (Fig. 2A and 2B) is etched using a plasma of fluorocarbon-based gas-here, $CF_4$ gas-and plasma of additive gases of Ar and $O_2$. As shown in this drawing the $SiO_2$ film 17 is formed on a substrate 16 by way of example, and a

mask pattern 18 made of a chosen photoresist material is further formed thereon allowing the resulting structure to be subject to an etching treatment by use of the etching apparatus shown in Fig. 1. At this time the etching gas attempts to dissociate in the plasma hitting the target wafer so that the etching progresses accordingly. When this is done, any unnecessary deposits left adhered to the inner walls of the apparatus with the to-be-etched object being as the cause thereof may become oxides containing silicon and chemical compounds containing organic substance.

Incidentally, a gas used for dry cleaning is aimed at creation of chemical compounds of increased vapor pressure by reaction with the deposits to be removed away, which will finally be removed through vaporization and vacuum evacuation. Assuming for instance that the deposits are carbon compounds, a plasma of $O_2$ gas is applied thereto permitting vaporization thereof to CO or $CO_2$ gases for removal. To do this, the prior art approach as taught by PUJPA No. 7-508313 indicated in the introductory part of the description is designed to employ a cleaning gas consisting of the mixture of a chlorine-based gas and oxygen-based gas. Mixing oxygen thereinto may improve the efficiency as a whole by disconnecting or separating carbon from chemical compounds containing therein metal and chlorine as well as organic substance while cleaning the metal by chlorine.

When etching the $SiO_2$ film as used in this embodiment, cleaning is typically done using a mixture or combination of a fluorine-based gas and oxygen-based gas. However, as stated supra, the plasma originated from the etching gas attempts, in addition to etching the substrate surfaces 17, 18 to be etched, to hit also the materials of apparatus internal parts or components such as for example the clamper 8 and Earth plate 7 resulting in an increase in amount of undesired secondary etching products devotable to creation of the deposition film 13, which products may include in addition to the reaction products of the to-be-etched material either the ion sputtered products of the apparatus internal component materials or chemical compounds of such apparatus materials and of the etching gas used herein.

Typically, alumina components are employed in plasma-applied semiconductor manufacturing apparatus including the etching apparatus. In this embodiment (the example shown in Fig. 2) unnecessary deposits stacked or adhered to the apparatus inner walls may be left in the form of organic compounds of the to-be-etched $SiO_2$ material and of resist material which are originated from the to-be-etched object per se and also in the form of alumina as a result of ion sputtering due to the fact that the clamper 8 as one of the alumina components inside the apparatus is hit by a plasma. Part of this may be attached and adhered in the form of aluminum fluoride by reaction of fluorine during etching. The prior art dry cleaning architecture merely comes with a cleaning treatment with respect to limited materials such as $SiO_2$ and organic compounds of resist materials. To be more specific, the prior art fails to take into consideration in any way the depositability of either sputtered products of the apparatus internal component materials or chemical compounds of such apparatus materials and etching gas; obviously, the prior art does not take account of how a cleaning is to be done therefor. Accordingly, these might be finally left as the cause for generation of contaminants.

According to the present invention, it becomes possible, by adding to the dry etching process both the step of removing etching reaction products and the step of removing any chemical compounds of the apparatus inside component materials and etching gas(es), to successfully remove away also the deposits made of such compounds of the apparatus internal component materials which have been long ignored in the conventional dry cleaning technology, which in turn leads to capability of improving the cleaning effect while simultaneously increasing the contaminant generation suppression effect.

The illustrative embodiment is specifically designed to add as the apparatus inside material cleaning treatment a cleaning step using a mixture gas of $BCl_3$ and $Cl_2$. Aluminum attachments may be effectively removed away by production of $AlCl_3$ of high vapor pressure using a $Cl_2$ gas plasma. However, in cases where such aluminum is of oxide or fluoride, the plasma of $Cl_2$ alone is incapable of producing $AlCl_3$ rendering it impossible to effectuate any intended removal by cleaning due to the fact that the interatomic bonding energy of Al-O and Al-F remains greater than the interatomic bonding energy of Al-C. In view of this, a specifically arranged gas containing therein B such as a $BCl_3$ gas, which has its interatomic bonding energy with respect to fluorine and oxygen as greater in value than the interatomic bonding energy of Al-O and Al-F, is mixed into the $Cl_2$ gas thereby removing O and F out of Al-O and Al-F to thereby render effective the cleaning by $Cl_2$. This may in turn enable achievement of successful removal of ion sputtered products of the apparatus internal component materials along with removal of inherent etching reaction products.

Here, sequential execution of a cleaning using $O_2$ and sulphur hexafluoride ($SF_6$) and cleaning using a mixture gas of $BCl_3$ and $Cl_2$ may remarkably increase the cleaning effect inside the apparatus and also the contaminant suppression effect therein.

In the way discussed above, the cleaning effect within the apparatus may dramatically be improved by performing the dry cleaning process for removal of ion sputtered products of the apparatus internal member materials or any chemical compounds of such apparatus materials and an etching gas in addition to the dry cleaning for removal of reactive products with respect to the to-be-etched material. While in this embodiment the dry cleaning for such etching reaction products and the cleaning with respect to the apparatus internal member materials are done sequentially, the two cleaning

gases may alternatively be mixed together.

Next, another embodiment applying the principles of the present invention to tungsten lead wires will be explained in conjunction with Fig. 3 ( Fig. 3A and 3B ). As shown in Fig. 3, a tungsten lead wire layer 19 is formed on the substrate 16 while a mask pattern 18 made of a chosen photoresistive material is formed thereon; the resulting structure is then subject to an etching process in the etching apparatus shown in Fig. 1. For such tungsten a plasma of $SF_6$ gas is used to facilitate progression of an etching required.

During the above process any unnecessary deposits can be left adhered to the apparatus inner walls in the form of chemical compounds containing therein tungsten, fluorine and organic substance, and further aluminum oxide as ion-sputtered during the clamper 8 that is one of the alumina components inside the apparatus is being hit by a plasma. Part of this is in the form of aluminum fluoride due to the plasma of $SF_6$ gas during etching. Here, both the cleaning using $SF_6$ and the cleaning using the mixture gas of $BCl_3$ and $Cl_2$ were done in a sequential manner. $SF_6$ may exhibit some cleaning effects with respect to tungsten and organic substance also. The cleaning using the $BCl_3/Cl_2$ mixture gas exhibits cleaning effects with respect to aluminum oxide and aluminum fluoride as has been explained in conjunction with the first embodiment. This cleaning is advantageous in extremely improving the contaminant suppression effect. As in the first embodiment, the cleaning effect may be noticeably enhanced by performing both the dry cleaning process for removal of reaction products with respect to the etching material and also the dry cleaning with respect to the apparatus internal member materials.

An explanation will now be given of a further embodiment incorporating the principles of the present invention. Here, an exemplary case will be discussed wherein the present invention is applied to the case of etching aluminum lead wires as shown in Fig. 4 (Fig. 4A and 4B ).

Recently, most metal lead wires come with a lamination structure having a barrier metal layer 21 associated therewith as depicted in Fig. 4, rather than a single aluminum film structure, which permits use of a plurality of kinds of etching gases during etching processes thereof. This is for achieving superior anti-electromigration characteristics and diffusion barrier characteristics. Exemplarily explained herein is the case of etching a lamination film structure consisting essentially of an aluminum lead-wire layer 20 and titanium-tungsten (TiW) barrier metal 21. As stated previously, etching is performed in a way such that a chosen chemical compound of high vapor pressure relative to the material to be etched is formed letting the etching progress. In this case the first layer 20 made of aluminum is etched by altering to $AlCl_3$ of high vapor pressure using a $Cl_2$ gas. When this is done, Al or $AlCl_x$ can be attached and adhered for deposition to the apparatus inner walls, including several structure components of the processing room, such as for example the quartz bell jar 3, main chamber 4, gas introduction port 15, and clamper 8. Thereafter, the second layer of $TiW_2O$ is processed by a $SF_6$ plasma; at this time, Ti or tungsten (W) might be stacked and adhered to the apparatus inner walls and/or the constituent components of the processing room thereof.

Typically, in cases of cleaning Al or $AlCl_x$ and of cleaning Ti, the $Cl_2$ plasma may be used for removal thereof by altering them to $AlCl_3$ and TiCl of higher vapor pressure. In the case of cleaning W, a plasma of fluoride gas, such as for example $SF_6$ plasma, is employable to remove the same by altering it to $WF_6$ of higher vapor pressure.

Unfortunately, in cases where the film for configuration of an intended lead wire pattern is of lamination film structure rather than a single film structure, resultant deposition films left adhered to the apparatus inner walls and the constituent components of the processing room are not a simple form but in the "complex" form of chemical compounds with such gasses because of use of a plasma of plural etching gases and also use of multiple cleaning gases.

More specifically, any possible additive deposits are such that:

1) Al or $AlCl_x$ is attached for deposition during etching of the first layer. The resultant deposits are altered by the $SF_6$ plasma to aluminum fluoride during the TiW etching of the second layer. Thereafter, $TiW_2O$ of the second layer is processed by $SF_6$ plasma, which would result in attachment and deposition of Ti or W onto the apparatus inner walls and the structure components of the processing room.

2) Al and $AlCl_x$ as deposited during etching of the first layer are further accelerated in production of aluminum fluoride during the $SF_6$ plasma cleaning process for removal of W, which is a deposit during the TiW etching of the second layer.

3) A plasma originated from the etching gas or cleaning gas attempts to hit the apparatus internal component materials, i.e. aluminum components as typically employed for the apparatus inside components, resulting in attachment and deposition onto the apparatus inner walls by ion sputtering action in the form of aluminum oxide.

4) The aluminum oxide left adhered to the apparatus inner walls by such plasma's ion sputtering action is then altered in part to aluminum fluoride by the $SF_6$ plasma during the TiW etching of the second layer.

5) The aluminum oxide left adhered to the apparatus inner walls due to the plasma's ion sputtering action is partly altered to aluminum fluoride due to $SF_6$ plasma during W cleaning.

In the way discussed above, where a multi-layered

lead wire is to be etched, certain plasma of an etching gas behaves during etching of one lead wire layer to alter certain deposits as stacked to the apparatus inner walls during etching of another lead wire layer to specific chemical compounds hard to be removed away. Furthermore, during cleaning deposits of a certain element, the plasma of a cleaning gas used herein attempts to alter those deposits of another element to compounds hard to be removed. These can disadvantageously serve to provide a bar to accomplishment of intended cleaning performance.

Moreover, the plasma of etching gas and that of cleaning gas will possibly hit the apparatus inside materials also, which results in attachment of ion sputtered products of such apparatus materials to inside of the apparatus. These may also become chemical compounds with the etching gas and cleaning gas. These can raise a serious bar to achievement of an intended cleaning in both performance and reliability.

According to the present invention, the dry cleaning process is specifically added with a cleaning step using a specific gas containing therein a chosen material having the interatomic bonding energy with the etching gas elements which energy is greater in value than the interatomic energy between the element(s) constituting the to-be-etched object and those constituting the etching gas. This makes it possible to successfully remove any unnecessary deposits as discussed at Paragraph 1). Specifically, it becomes possible to remove away those aluminum fluorides which are altered by $SF_6$ plasma during the TiW etching of the second layer from Al as deposited during etching of the first layer.

Another advantage of the invention lies in capability of removing the deposits discussed supra at Paragraph 3) because of the fact that the step of removing ion sputtered products of the apparatus internal member materials is added along with the step of removing etching reaction products. This in turn makes it possible to remove any ion sputtered products of aluminum components used as internal parts or components of the etching apparatus employed.

Furthermore, the dry cleaning process is specifically arranged to include a cleaning step using a specific gas containing therein a material having the interatomic bonding energy with the gas elements of the cleaning step, which energy is greater in value than the interatomic bonding energy between inherent materials, including the to-be-etched material and apparatus component materials, and the elements constituting the cleaning gases at other steps. This may advantageously serve to enable successful removal of those deposits of the kinds as discussed at Paragraphs 2) and 4) to 5). In other words, it becomes possible to remove any deposits which have become aluminum fluoride due to the $SF_6$ plasma during the W cleaning.

More practically, use of $Cl_2$ plasma alone is unable to remove by cleaning the aluminum fluoride which has been created by alteration of aluminum to fluoride due to the $SF_6$ plasma as used during the etching and cleaning. Arranging the dry cleaning process so as to employ as the cleaning gas a mixture of $Cl_2$ and $BCl_3$ added thereto-the latter is a chosen gas containing therein the material B having the interatomic bonding energy with fluorine which energy is greater in value than the interatomic bonding energy between fluorine for use in etching and cleaning and aluminum used as the to-be-etched material--may enable separation of F from Al-F, which in turn renders effective the cleaning using $Cl_2$.

B is such that the interatomic bonding energy of B-O is greater than that of aluminum oxide Al-O which is the ion sputtered products of the apparatus internal member material(s). Accordingly, mixing a B-contained gas and $BCl_3$ into $Cl_2$ gas enables separation of O from Al-O rendering more effective the cleaning by $Cl_2$. This makes it possible to remove any ion sputtered products of the apparatus internal member materials also.

The aforesaid cleaning process for certain the films deposited by reaction with the etching and cleaning gases at the next step as required due to the multilayer lamination film structure may be performed before and/or after the cleaning process for etching reaction products alone.

It must be noted that although the illustrative embodiments of the invention have been described based on specific examples directed to use of the microwave etching apparatus, the invention should not exclusively be limited thereto and may alternatively be modifiable for use in other applications with etching apparatus of any type as far as it is designed to employ a plasma to clean out deposits on the apparatus inner walls, including but not limited to parallel-flat plate type etching apparatus, induction-coupled etching apparatus, or CVD apparatus, while offering similar technical advantages discussed previously.

As has been described above, according to the present invention, it becomes possible to effectively remove any deposition films left adhered to the inner walls of manufacturing apparatus employed. This makes it possible to eliminate peel-off or abruption of such deposition films due to an increase in thickness thereof (increase in processing number) and also dust production as originated therefrom, which in turn enables improvement of the production yield during manufacturing processes while simultaneously increasing the working efficiency of manufacturing apparatus used.

While the invention has been described with reference to specific embodiments, the description is illustrative of the invention and is not to be construed as limiting the invention. Various modifications and applications may occur to those skilled in the art without departing from the true spirit and scope of the invention.

## Claims

1. A plasma treatment method for performing an etch-

ing treatment and dry cleaning processing with respect to a wafer within plasma etching apparatus, characterized in that

said dry cleaning processing has a dry cleaning process using a cleaning gas for removal of etching reaction products and a cleaning gas for removal of either ion sputtered matter of an internal member material of the etching apparatus or a chemical compound of the etching apparatus internal member material and an etching gas.

2. A wafer plasma treatment method for performing an etching treatment and dry cleaning processing within plasma etching apparatus, characterized in that

said dry cleaning processing comprises the steps of removing etching reaction products, and removing a chemical compound of a material of an internal member of the etching apparatus and an etching gas used.

3. A wafer plasma treatment method for performing an etching treatment and dry cleaning processing within plasma etching apparatus, characterized in that

said dry cleaning processing comprises the step of:
cleaning using a chosen gas containing therein a material with its interatomic bonding energy with respect to elements constituting a gas used in the process of etching treatment, which energy is greater in value than the interatomic bonding energy between elements constituting a material to be etched and elements constituting the gas for use in the etching treatment process.

4. A wafer plasma treatment method for performing an etching treatment and dry cleaning processing within plasma etching apparatus, characterized in that

said dry cleaning process has the step of performing a cleaning with respect to a deposited compound left adhered to inside of the etching apparatus by use of a gas containing therein a material having its interatomic bonding energy with respect to at least one of elements constituting said compound, which energy is greater in value than the interatomic bonding energy between elements constituting said compound.

5. A dry cleaning method of plasma etching apparatus to be performed using plasma of a plurality of kinds of gases, characterized by comprising:

a first cleaning step; and
a second cleaning step using a gas containing therein a material having its interatomic bonding energy with respect to elements constituting a gas as used in said first cleaning step, which energy is greater in value than the interatomic bonding energy between elements constituting a material to be etched and elements constituting the gas used in the first cleaning step.

6. A dry cleaning method of plasma etching apparatus characterized in that the step of performing dry etching has:

a cleaning step of a gas containing therein a material having its interatomic bonding energy with respect to elements constituting a gas used for etching, which energy is greater in value than the interatomic bonding energy between elements constituting an internal member material of the etching apparatus and elements constituting a gas used in the etching step.

7. A method for dry cleaning a material to be processed within plasma etching apparatus by using plasma of a plurality of kinds of gases, characterized by comprising:

a first cleaning step; and
a second cleaning step using a gas containing therein a material having its interatomic bonding energy with respect to elements constituting a gas used in the first cleaning step, which energy is greater in value than the interatomic bonding energy between elements constituting a material of an internal member of the etching apparatus and elements constituting the gas used in the first cleaning step.

8. A dry cleaning method using a plasma of a gas containing therein any one of fluorine, chlorine and oxygen during an etching process or a process of cleaning inside of the etching apparatus while a material to be etched contains metal oxide, characterized in that

the dry cleaning process includes at least one cleaning step employing a mixture gas of a boron-contained gas and chlorine.

9. A dry cleaning method using a plasma of a gas containing therein at least one of fluorine, chlorine and oxygen during an etching process or a process of cleaning inside of etching apparatus while a material to be etched includes any one of aluminum, tungsten, copper and platinum, characterized in that

the dry cleaning process includes at least one cleaning step making use of a mixture gas of boron-contained gas and chlorine.

10. Etching processing apparatus comprising its constituent components inside thereof including those made of a metallic material having oxygen-contained ceramics, quartz, and surface oxidation film,

characterized in that

the dry cleaning process including at least one cleaning step using a boron-contained gas or a mixture gas containing such boron-contained gas.

11. The cleaning method according to any one of the preceding claims 1 to 9, characterized in that the plasma cleaning is selectively executable depending on a given number.

12. A method for manufacturing a semiconductor device, characterized by cleaning inside of manufacturing apparatus using the cleaning method according to any one of claims 1 to 10, and thereafter performing a surface processing of a semiconductor wafer by use of such manufacturing apparatus.

13. A plasma treatment method for performing a plasma treatment with respect to a material to be processed within processing apparatus, characterized in that

the method comprises a dry cleaning process after completion of said plasma treatment, and in that said dry cleaning process is the process of performing a dry cleaning processing by use of a cleaning gas for removal of etching reaction products and a cleaning gas for removal of either ion-sputtered matter of an internal member material of the processing apparatus or chemical compound of the processing apparatus internal member material and an etching gas.

14. A plasma treatment method for performing a plasma treatment with respect to a material to be processed within processing apparatus, characterized in that

the method comprises a dry cleaning step after completion of said plasma treatment, and in that said dry cleaning process includes the step of removing an etching reaction product, and removing either ion sputtered matter of an internal member material of the processing apparatus or chemical compounds of the processing apparatus internal member material and an etching gas.

FIG. 1

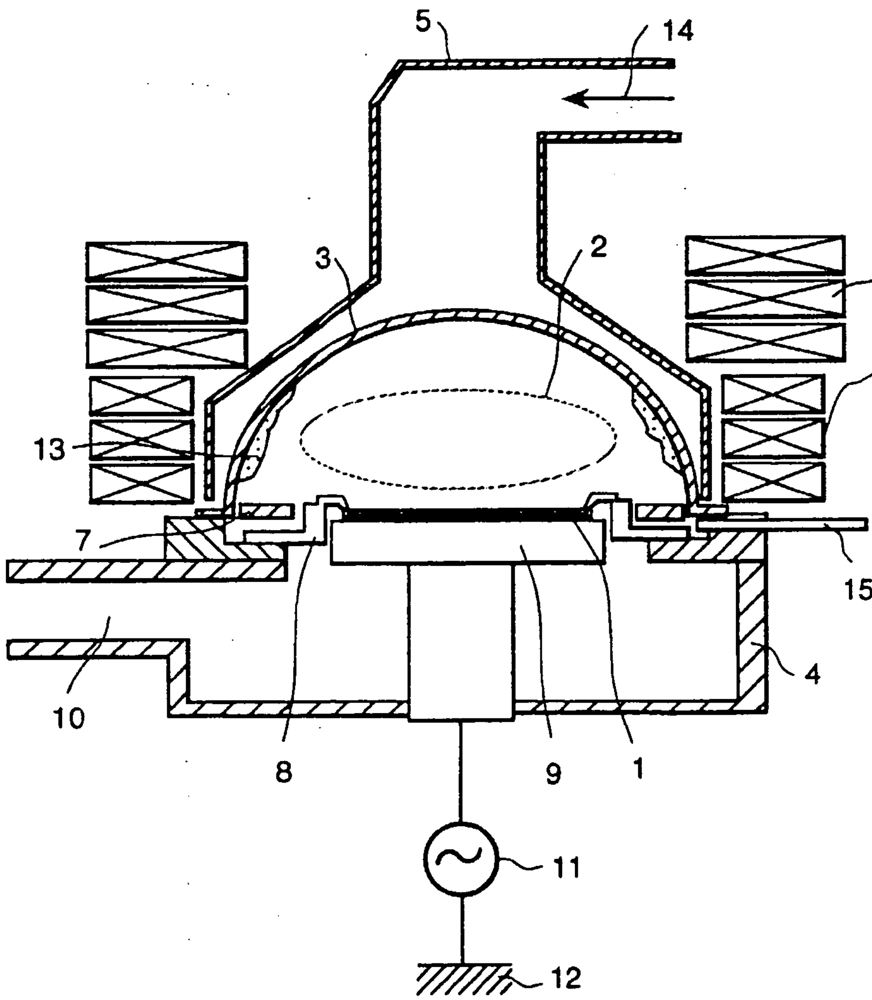


*FIG. 2A*

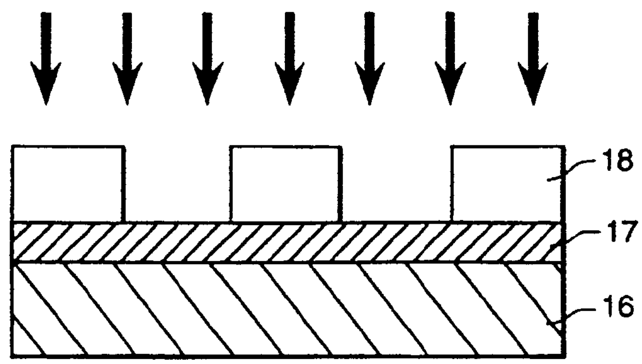



*FIG. 2B*

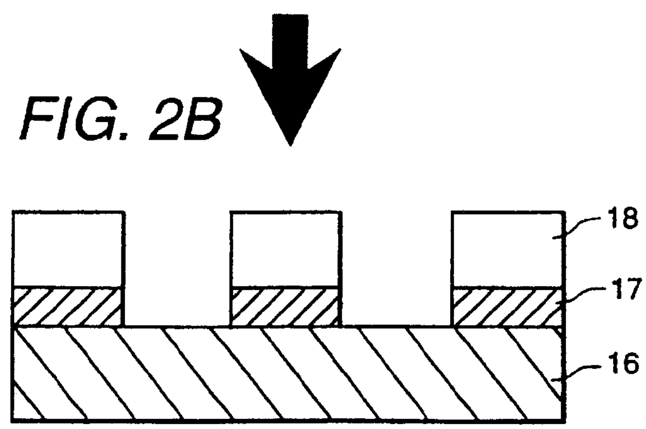


FIG. 3A

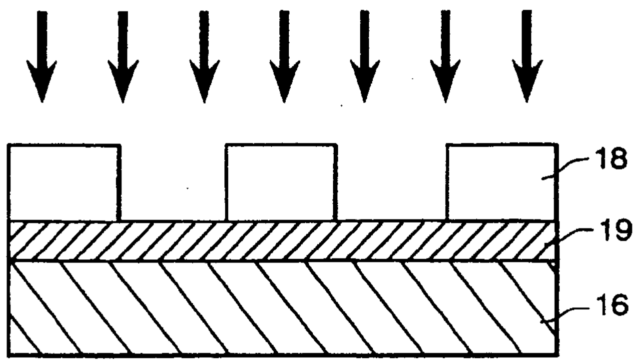



FIG. 3B

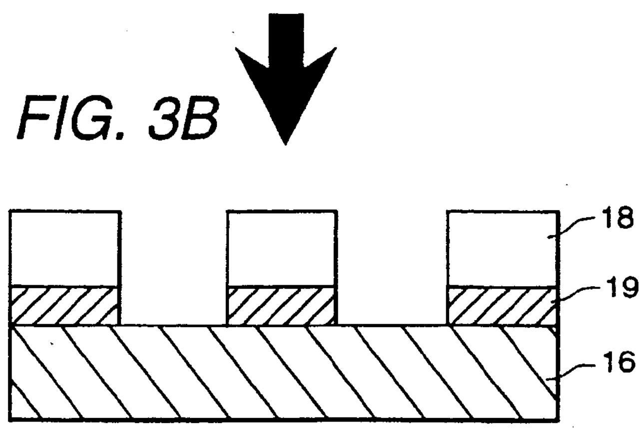


FIG. 4A

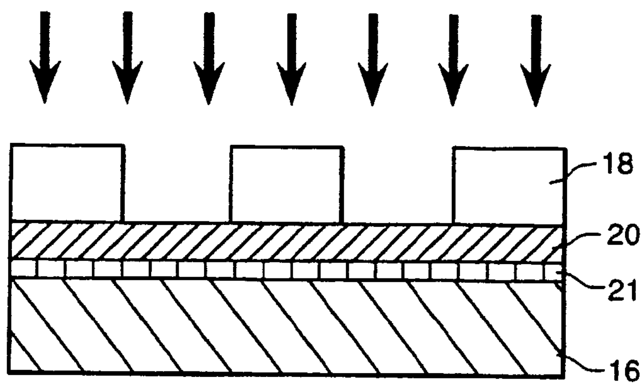
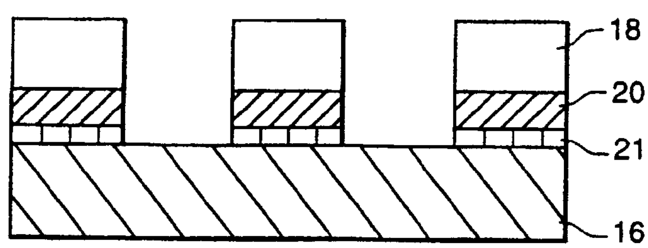



FIG. 4B



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(71) Applicant: Hitachi, Ltd.
Chiyoda-ku, Tokyo 101-8010 (JP)

(72) Inventors:
- Kitsunai, Hiroyuki
Niihari-gun, Ibaraki 315-0055 (JP)
- Tsumaki, Nobuo
Ushiku-shi, Ibaraki 300-1236 (JP)
- Kakuta, Shigeru
Yokohama-shi, Kanagawa 244-0817 (JP)
- Nojiri, Kazuo
Higashimurayama-shi, Tokyo 189-0012 (JP)
- Takahashi, Kazue
Kudamatsu-shi, Yamaguchi 744-0006 (JP)

(74) Representative:
Paget, Hugh Charles Edward et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

# (54) Plasma treatment method and manufacturing method of semiconductor device

(57) The dry cleaning method is capable of removing deposition films left adhered to the inner walls of semiconductor manufacturing apparatus i.e. removing dust production sources. To this end, the dry cleaning process includes a step of removing either ion sputtered matter or products of the internal member materials of the apparatus or chemical compounds of such apparatus internal member materials and of an etching gas, in addition to a step of removing etching reaction products. It thus becomes possible to eliminate dust generation due to peeling off of deposition films with an increase in number of wafers being processed, which in turn increases the manufacturing yield and working efficiency of the manufacturing apparatus.

EP 0 871 211 A3

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## PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 98 30 2036

### DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X | PATENT ABSTRACTS OF JAPAN vol. 097, no. 004, 30 April 1997 (1997-04-30) & JP 08 319586 A (NEC YAMAGATA LTD), 3 December 1996 (1996-12-03) * abstract * -& US 5 817 578 A (NEC) 6 October 1998 (1998-10-06) * column 4, line 48 - line 66 * * column 5, line 35 - line 40 * | 8,9,12 | H01L21/306 C23C16/44 |
| D,A | PATENT ABSTRACTS OF JAPAN vol. 015, no. 219 (E-1074), 5 June 1991 (1991-06-05) -& JP 03 062520 A (HITACHI LTD), 18 March 1991 (1991-03-18) * abstract * | | |
| A | PATENT ABSTRACTS OF JAPAN vol. 096, no. 004, 30 April 1996 (1996-04-30) & JP 07 335626 A (HITACHI LTD), 22 December 1995 (1995-12-22) * abstract * | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) C23C H01L |

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### INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 21 September 1999 | Szarowski, A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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INCOMPLETE SEARCH SHEET C

Application Number
EP 98 30 2036

Claim(s) searched completely:
none

Claim(s) searched incompletely:
8,9,12

Claim(s) not searched:
1-7,10-11,13-14

Reason for the limitation of the search:

The claims do not meet requirements of Art 84 EPC. The claims lack concision and support by the description. The claims 1-7 are defined by the result to be achieved, guidelines CIII 4.7. The subject matter of claims 3-7 is not comprehensible. The subject matter of claim 10 is obscure, guidelines CIII 4.8.a.

The search was limited to a process for cleaning a chamber with the following steps:
SF6 followed by BCl3+Cl2 or SF6+BCl3+Cl2 mixture.

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# PARTIAL EUROPEAN SEARCH REPORT

Application Number
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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
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| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |

EPO FORM 1503 03.82 (P04C10)

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 30 2036

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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| JP 07335626 A | 22-12-1995 | NONE | |
| JP 08088215 A | 02-04-1996 | NONE | |
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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82